

S/N Unknown

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: Thomas R. Mallen

Examiner: R. Lovering

Serial No.: Unknown

Group Art Unit: 1712

Filed: Herewith

Docket: 1190.322US2

Title: IMPROVED COATING COMPOSITIONS

PRELIMINARY AMENDMENT

BOX PATENT APPLICATION

Commissioner for Patents

Washington, D.C. 20231

Dear Sir:

Prior to taking up the above-identified divisional patent application for examination, please amend the application as follows:

In the Specification

Please make the paragraph substitutions indicated in the appendix entitled Clean Version of Amended Specification Paragraphs. The specific changes incorporated in the substitute paragraphs are shown in the following marked-up versions of the original paragraphs.

On page 1 after the title, please add the following:

-- Cross-Reference to Related Application

This application is a divisional application of U.S. Patent Application No. 09/260,958, filed March 2, 1999, which is incorporated herein by reference. -

Please amend the paragraph at page 5, lines 20-28, through page 6, lines 1-2, as follows:

Any epoxy resin may be included in the epoxy resin-based polymer. Typically, the epoxy resin includes glycidyl polyethers having one or more epoxide group per molecule (i.e., glycidyl ethers containing an average of at least one and generally greater than 1.0 epoxy groups per molecule). The glycidyl polyethers commonly have an average of about 2.0 to about 2.5 epoxide

groups per molecule. Diglycidyl ethers of dihydric phenols, such as is Bisphenol A (p,p'-dihydroxy-2,2-diphenyl propane), are particularly suitable. The epoxy resins typically used in the present invention may be derived from the reaction of dihydric phenol and an epichlorohydrin, such as [epichlorohydrin]epichlorohydrin. Epoxy resins based on Bisphenol A and epichlorohydrin are especially suitable, because these compounds have been approved in the United States by the Food and Drug Administration for use in can coatings.

Please amend the paragraph at page 7, lines 8-22, as follows:

The film-forming component of the coating compositions of the present invention also contains polyvinyl alcoholic-containing phenolic resin. This resin may be made by reacting a mixture including a phenol, an aldehyde and a polyvinyl alcoholic compound, such as specified in U.S. Patent Application Serial No. 09/032,907 filed on March 2, 1998, by [Wang, et al., entitled "Inhibiting Scale in Vinyl Chloride Polymerization" (hereinafter "Wang et al.")] Warakomski, entitled "Phenolic Thermosetting Resins Containing Polyols" (hereinafter "Warakomski"), which is incorporated herein by reference. The phenolic resin can be formed by reacting a phenol and formaldehyde in the presence of a polymerization catalyst, and a polyvinyl alcoholic compound. The phenol may include an alkyl phenol, a bisphenol or mixtures thereof. Examples of suitable alkyl phenols include those containing from 7 to 20 carbon atoms, such as p-tertiary octyl phenol, p-tertiary butylphenol, nonyl phenol and dodecyl phenol. Examples of suitable bisphenols include Bisphenol A (4,4'-isopropylidenediphenol), Bisphenol F (4,4'-methylenebisphenol) and Bisphenol S (4,4'-sulfonylbisphenol). Bisphenol A is especially suitable for use in the present invention. The molar ratio of formaldehyde to the phenol is generally about 1:1 to about 1:3, and preferably about 1:1.5 to about 1:2.5.

Please amend the paragraph at page 7, lines 24-29, through page 8, lines 1-4 as follows:

The polyvinyl alcoholic compound includes polyvinyl alcohols and protected versions thereof, such as complete or partial esters of polyvinyl alcohol and acetals derived from polyvinyl

alcohol including polyvinyl butyral and polyvinyl formal. The polyvinyl alcoholic compound can be produced by polymerizing a vinyl ester to produce a polyvinyl ester. The ester groups are then [hydrolized]hydrolyzed either partially or fully to generate [hydroxyl]hydroxyl groups. The hydroxyl groups may be [derivitized]derivatized by reaction with an aldehyde or ketone to produce acetal functional groups, which is, for example, one form of a protected polyvinyl alcohol. Particularly suitable polyvinyl alcoholic compounds for use in the present invention include partially hydrolyzed polyvinyl acetates, a commercial example of which is grade 205 polyvinyl alcohol sold by Air Products.

Please amend the paragraph at page 16, lines 3-12, as follows:

The resinous material was allowed to cool to 94_°C. Upon cooling, 45.5 parts Durez 33-345, a [commerical]commercial polyvinyl alcoholic-containing resin (Occidental Chemical Corporation, Dallas, TX), was added, followed by agitation for 30 minutes. The heating mantle was set at 75_°C, and water dispersion was initiated by adding 682.9 parts deionized water at a rate of 25 ml every 10 minutes. Inversion occurred approximately one and one-half hours after commencement of the water addition, at which time the heating mantle was removed. The water addition continued until completion and the dispersion was agitated for one and one-half hours with passive cooling to ambient temperature. The final composition contained 44.1% solids and had an average particle size of 0.21 micrometers.

In the Claims

Please cancel claims 1-21, and 25-27, without prejudice; amend claims 22 and 23; and add claims 28-45. Please substitute the claim set in the appendix entitled Clean Version of Pending Claims for the previously pending claim set. The substitute claim set is intended to reflect cancellation of claims 1-21 and 24-27, amendment of previously pending claims 22 and 23, and addition of new claims 28-45. The specific amendments to individual claims are detailed in the following marked up set of claims.

22. (Amended) A method of coating a metal substrate comprising:
- a) applying a coating composition [of claim 1] on to at least one surface of the metal substrate to form a coating layer on the surface, wherein the coating composition comprises a film forming component comprising a product formed by reacting a mixture including
 - i) a carboxy functional polymer, a hydroxy functional polymer, or a mixture thereof, and
 - ii) an epoxy resin; and
 - b) heating the coated metal substrate such that the coating layer cures to form a cured film on the substrate surface.
23. (Amended) A composite material comprising a metal substrate having at least one surface covered with a cured film, wherein the cured film is formed by:
- a) coating the substrate surface with [the coating composition of claim 1] a coating composition comprising a film-forming component which includes a product formed by reacting a mixture including
 - i) a carboxy functional polymer, a hydroxy functional polymer, or a mixture thereof, and
 - ii) an epoxy resin; and a polyvinyl alcoholic-containing phenolic resol resin;
and
 - b) heating the coated metal substrate.

Please add the following new claims:

28. The method of claim 22, wherein the carboxy functional polymer includes a copolymer of at least one ethylenically unsaturated carboxylic acid and at least one copolymerizable nonionic monomer.
29. The method of claim 22, wherein the carboxy functional polymer is a copolymer of

acrylic acid, styrene and ethyl acrylate or a copolymer of methacrylic acid, styrene and ethyl acrylate, or a mixture thereof.

30. The method of claim 22, wherein the carboxy functional polymer has an acid number of about 200 to about 530.

31. The method of claim 22, wherein the carboxy functional polymer has a glass transition temperature of no more than about 110 degrees C and a weight average molecular weight of about 5,000 to about 30,000.

32. The method of claim 22, wherein the epoxy resin includes glycidyl ether of dihydric phenol.

33. The method of claim 22, wherein the epoxy resin has an epoxide equivalent weight of about 1,000 to about 5,000.

34. The method of claim 22, wherein the epoxy resin is the reaction product of a mixture including aliphatic diacid, aromatic diacid, or a mixture thereof, and glycidyl ether of dihydric phenol.

35. The method of claim 22, wherein the polyvinyl alcohol-containing phenolic resol resin is the reaction product of a mixture including: phenolic compound; formaldehyde; and polyvinyl alcoholic compound.

36. The method of claim 22, wherein the resol resin comprises about 1 wt. % to about 25 wt. % of the polyvinyl alcoholic compound.

37. The method of claim 22, wherein the carboxy or hydroxy functional polymer is prepared

by polymerization of an ethylenically unsaturated monomer or monomer blend, wherein the monomer or monomer blend includes at least one monomer containing a carboxylic acid group or at least one monomer containing a hydroxy group, in the presence of the epoxy resin.

38. The method of claim 37, wherein the functional polymer is the carboxy functional polymer and includes a copolymer of at least one ethylenically unsaturated carboxylic acid and at least one copolymerizable nonionic monomer.

39. The method of claim 38, wherein the ethylenically unsaturated carboxylic acid is acrylic acid, methacrylic acid or a mixture thereof and the nonionic monomer is a lower alkyl acrylate, a lower alkyl methacrylates, a hydroxy alkyl acrylate, a hydroxy alkyl methacrylate, styrene, alkyl-substituted styrene, vinyl acetate, acrylonitrile or a mixture thereof.

40. The method of claim 39, wherein the functional polymer is a copolymer of acrylic acid, styrene and ethyl acrylate or a copolymer of methacrylic acid, styrene and ethyl acrylate, or a mixture thereof.

41. The method of claim 40, wherein the product comprises a graft copolymer of the epoxy resin.

42. The method of claim 41, wherein the product comprises a graft copolymer of the epoxy resin, an ungrafted addition polymer and an ungrafted epoxy resin.

43. The material of claim 23, wherein the carboxy functional polymer includes a copolymer of at least one ethylenically unsaturated carboxylic acid and at least one copolymerizable nonionic monomer, has a glass transition temperature of no more than about 110 degrees C, and has a weight average molecular weight of about 5,000 to about 30,000.

44. The material of claim 23, wherein the epoxy resin is the reaction product of a mixture including aliphatic diacid, aromatic diacid, or a mixture thereof, and glycidyl ether of dihydric phenol, and wherein the polyvinyl alcohol-containing phenolic resol resin is the reaction product of a mixture including: phenolic compound; formaldehyde; and polyvinyl alcoholic compound.

45. The material of claim 23, wherein the functional polymer is a copolymer of acrylic acid, styrene and ethyl acrylate or a copolymer of methacrylic acid, styrene and ethyl acrylate, or a mixture thereof.

In the Abstract

Please make the substitution indicated in the appendix entitled Clean Version of Amended Abstract. The specific change incorporated in the substitute Abstract is shown in the following marked-up version of the original Abstract.

Abstract

Coating composition including a film-forming component, further including (a) a product formed by reacting a mixture including carboxy functional polymer, [hyrdroxy]hydroxy functional polymer, or a mixture thereof, or ethylenically unsaturated monomer, with epoxy resin, and (b) a polyvinyl alcoholic-containing phenolic resol resin. Also provided is a method of coating a metal substrate with said coating composition. Further provided is a composite material comprising a metal substrate having at least one surface covered with a cured film of the coating composition.

Remarks

After the amendments herein, claims 22-23 and 28-45 are pending in the application. The amendments to the specification are to correct typographical errors. The amendments to claims 22 and 23 are to incorporate the subject matter from cancelled claim 1. New claims 28-45 have

been added to define preferred embodiments. These claims are supported by the application as filed. No new subject matter has been added

Applicant notes that the amendments to claims 22 and 23 were made to incorporate the subject matter from cancelled claim 1; the amendments did not narrow the scope of the claims. Thus, upon allowance, these claims are entitled to a full scope of equivalents.

When the Examiner takes this application up for the first Office Action, consideration of these amendments and remarks is respectfully requested. The Examiner is invited to telephone Applicant's attorney (612-373-6968) to facilitate prosecution of this application.

Respectfully submitted,

THOMAS R. MALLIN

By his Representatives,

SCHWEGMAN, LUNDBERG, WOESSNER &
KLUTH, P.A.
P.O. Box 2938
Minneapolis, MN 55402
(612) 373-6968

Date March 15, 2002

By William F. Prout
William F. Prout
Reg. No. 33,995

"Express Mail" mailing label number: EV041075944US

Date of Deposit: March 18, 2002

This paper or fee is being deposited on the date indicated above with the United States Postal Service pursuant to 37 CFR 1.10, and is addressed to the Commissioner for Patents, Box Patent Application, Washington, D.C. 20231.

CLEAN VERSION OF ABSTRACT

IMPROVED COATING COMPOSITIONS

Applicant: Thomas R. Mallen
Serial No.: Unknown

Abstract

Coating composition including a film-forming component, further including (a) a product formed by reacting a mixture including carboxy functional polymer, hydroxy functional polymer, or a mixture thereof, or ethylenically unsaturated monomer, with epoxy resin, and (b) a polyvinyl alcoholic-containing phenolic resol resin. Also provided is a method of coating a metal substrate with said coating composition. Further provided is a composite material comprising a metal substrate having at least one surface covered with a cured film of the coating composition.

2025 FEB 24 2500T

CLEAN VERSION OF AMENDED SPECIFICATION PARAGRAPHS

IMPROVED COATING COMPOSITIONS

Applicant: Thomas R. Mallen
Serial No.: Unknown

Cross-Reference to Related Application

This application is a divisional application of U.S. Patent Application No. 09/260,958, filed March 2, 1999, which is incorporated herein by reference.

Any epoxy resin may be included in the epoxy resin-based polymer. Typically, the epoxy resin includes glycidyl polyethers having one or more epoxide group per molecule (i.e., glycidyl ethers containing an average of at least one and generally greater than 1.0 epoxy groups per molecule). The glycidyl polyethers commonly have an average of about 2.0 to about 2.5 epoxide groups per molecule. Diglycidyl ethers of dihydric phenols, such as is Bisphenol A (p,p'-dihydroxy-2,2-diphenyl propane), are particularly suitable. The epoxy resins typically used in the present invention may be derived from the reaction of dihydric phenol and an epichlorohydrin, such as epichlorohydrin. Epoxy resins based on Bisphenol A and epichlorohydrin are especially suitable, because these compounds have been approved in the United States by the Food and Drug Administration for use in can coatings.

The film-forming component of the coating compositions of the present invention also contains polyvinyl alcoholic-containing phenolic resin. This resin may be made by reacting a mixture including a phenol, an aldehyde and a polyvinyl alcoholic compound, such as specified in U.S. Patent Application Serial No. 09/032,907 filed on March 2, 1998, by Warakomski, entitled "Phenolic Thermosetting Resins Containing Polyols" (hereinafter "Warakomski"), which is incorporated herein by reference. The phenolic resin can be formed by reacting a phenol and formaldehyde in the presence of a polymerization catalyst, and a polyvinyl alcoholic compound. The phenol may include an alkyl phenol, a bisphenol or mixtures thereof. Examples of suitable

alkyl phenols include those containing from 7 to 20 carbon atoms, such as p-tertiary octyl phenol, p-tertiary butylphenol, nonyl phenol and dodecyl phenol. Examples of suitable bisphenols include Bisphenol A (4,4'-isopropylidenediphenol), Bisphenol F (4,4'-methylenebisphenol) and Bisphenol S (4,4'-sulfonylbisphenol). Bisphenol A is especially suitable for use in the present invention. The molar ratio of formaldehyde to the phenol is generally about 1:1 to about 1:3, and preferably about 1:1.5 to about 1:2.5.

The polyvinyl alcoholic compound includes polyvinyl alcohols and protected versions thereof, such as complete or partial esters of polyvinyl alcohol and acetals derived from polyvinyl alcohol including polyvinyl butyral and polyvinyl formal. The polyvinyl alcoholic compound can be produced by polymerizing a vinyl ester to produce a polyvinyl ester. The ester groups are then [hydrolized]hydrolyzed either partially or fully to generate [hydroxyl]hydroxyl groups. The hydroxyl groups may be [derivitized]derivatized by reaction with an aldehyde or ketone to produce acetal functional groups, which is, for example, one form of a protected polyvinyl alcohol. Particularly suitable polyvinyl alcoholic compounds for use in the present invention include partially hydrolyzed polyvinyl acetates, a commercial example of which is grade 205 polyvinyl alcohol sold by Air Products.

The resinous material was allowed to cool to 94 °C. Upon cooling, 45.5 parts Durez 33-345, a [commerical]commercial polyvinyl alcoholic-containing resin (Occidental Chemical Corporation, Dallas, TX), was added, followed by agitation for 30 minutes. The heating mantle was set at 75 °C, and water dispersion was initiated by adding 682.9 parts deionized water at a rate of 25 ml every 10 minutes. Inversion occurred approximately one and one-half hours after commencement of the water addition, at which time the heating mantle was removed. The water addition continued until completion and the dispersion was agitated for one and one-half hours with passive cooling to ambient temperature. The final composition contained 44.1% solids and had an average particle size of 0.21 micrometers.

CLEAN VERSION OF PENDING CLAIMS

IMPROVED COATING COMPOSITIONS

Applicant: Thomas R. Mallen
Serial No.: Unknown

22. (Amended) A method of coating a metal substrate comprising:
- a) applying a coating composition on to at least one surface of the metal substrate to form a coating layer on the surface, wherein the coating composition comprises a film forming component comprising a product formed by reacting a mixture including
 - i) a carboxy functional polymer, a hydroxy functional polymer, or a mixture thereof, and
 - ii) an epoxy resin; and
 - b) heating the coated metal substrate such that the coating layer cures to form a cured film on the substrate surface.
23. (Amended) A composite material comprising a metal substrate having at least one surface covered with a cured film, wherein the cured film is formed by:
- c) coating the substrate surface with a coating composition comprising a film-forming component which includes a product formed by reacting a mixture including
 - iii) a carboxy functional polymer, a hydroxy functional polymer, or a mixture thereof, and
 - iv) an epoxy resin; and a polyvinyl alcoholic-containing phenolic resol resin; and
 - d) heating the coated metal substrate.
28. The method of claim 22, wherein the carboxy functional polymer includes a copolymer of at least one ethylenically unsaturated carboxylic acid and at least one copolymerizable nonionic monomer.

29. The method of claim 22, wherein the carboxy functional polymer is a copolymer of acrylic acid, styrene and ethyl acrylate or a copolymer of methacrylic acid, styrene and ethyl acrylate, or a mixture thereof.
30. The method of claim 22, wherein the carboxy functional polymer has an acid number of about 200 to about 530.
31. The method of claim 22, wherein the carboxy functional polymer has a glass transition temperature of no more than about 110 degrees C and a weight average molecular weight of about 5,000 to about 30,000.
32. The method of claim 22, wherein the epoxy resin includes glycidyl ether of dihydric phenol.
33. The method of claim 22, wherein the epoxy resin has an epoxide equivalent weight of about 1,000 to about 5,000.
34. The method of claim 22, wherein the epoxy resin is the reaction product of a mixture including aliphatic diacid, aromatic diacid, or a mixture thereof, and glycidyl ether of dihydric phenol.
35. The method of claim 22, wherein the polyvinyl alcohol-containing phenolic resol resin is the reaction product of a mixture including: phenolic compound; formaldehyde; and polyvinyl alcoholic compound.
36. The method of claim 22, wherein the resol resin comprises about 1 wt. % to about 25 wt. % of the polyvinyl alcoholic compound.

37. The method of claim 22, wherein the carboxy or hydroxy functional polymer is prepared by polymerization of an ethylenically unsaturated monomer or monomer blend, wherein the monomer or monomer blend includes at least one monomer containing a carboxylic acid group or at least one monomer containing a hydroxy group, in the presence of the epoxy resin.

38. The method of claim 37, wherein the functional polymer is the carboxy functional polymer and includes a copolymer of at least one ethylenically unsaturated carboxylic acid and at least one copolymerizable nonionic monomer.

39. The method of claim 38, wherein the ethylenically unsaturated carboxylic acid is acrylic acid, methacrylic acid or a mixture thereof and the nonionic monomer is a lower alkyl acrylate, a lower alkyl methacrylates, a hydroxy alkyl acrylate, a hydroxy alkyl methacrylate, styrene, alkyl-substituted styrene, vinyl acetate, acrylonitrile or a mixture thereof.

40. The method of claim 39, wherein the functional polymer is a copolymer of acrylic acid, styrene and ethyl acrylate or a copolymer of methacrylic acid, styrene and ethyl acrylate, or a mixture thereof.

41. The method of claim 40, wherein the product comprises a graft copolymer of the epoxy resin.

42. The method of claim 37, wherein the product comprises a graft copolymer of the epoxy resin, an ungrafted addition polymer and an ungrafted epoxy resin.

43. The material of claim 23, wherein the carboxy functional polymer includes a copolymer of at least one ethylenically unsaturated carboxylic acid and at least one copolymerizable nonionic monomer, has a glass transition temperature of no more than about 110 degrees C, and has a weight average molecular weight of about 5,000 to about 30,000.

RECEIVED 8-12-60

44. The material of claim 23, wherein the epoxy resin is the reaction product of a mixture including aliphatic diacid, aromatic diacid, or a mixture thereof, and glycidyl ether of dihydric phenol, and wherein the polyvinyl alcohol-containing phenolic resol resin is the reaction product of a mixture including: phenolic compound; formaldehyde; and polyvinyl alcoholic compound.

45. The material of claim 23, wherein the functional polymer is a copolymer of acrylic acid, styrene and ethyl acrylate or a copolymer of methacrylic acid, styrene and ethyl acrylate, or a mixture thereof

RECEIVED 2007-04-25